

Semiclassical transmission across transition states

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Abstract. It is shown that the probability of quantum-mechanical transmission across a phase space bottleneck can be compactly approximated using an operator derived from a complex Poincaré return map. This result uniformly incorporates tunnelling effects with classically-allowed transmission and generalises a result previously derived for a classically small region of phase space.

AMS classification scheme numbers: 81Q20, 81Q50, 81V55, 92E20

1. Introduction

There has recently been a resurgence of interest in the classical transition state theory of molecular reactions. Results that were historically restricted to two degrees of freedom [1, 2] have been generalised to arbitrary dimensions using the construction of normally hyperbolic invariant manifolds (or NHIM's) [3]-[7]. It is natural to ask how classical structure such as the NHIM is reflected in the quantum-mechanical problem, which corresponds to scattering from a multidimensional potential barrier.

An answer to this question has been offered in [8], where a description is given of quantum mechanical transport across a phase-space bottleneck using dynamics linearised around a certain complex periodic orbit. In using linearised dynamics these results are restricted to a classically small region of phase space and energies that are no larger than $O(\hbar)$ above a transmission threshold. In this paper it is shown how fully nonlinear dynamics may be incorporated in this approach, resulting in a description of transport which is not restricted to a small region of phase space or energy range above threshold. The current approach is based on a quantisation of a classical normal form Hamiltonian, although the final form can be expressed in such a way that explicit calculation of a normal form is not necessary.

To describe the result more concretely, let us consider a waveguide problem with configuration space coordinates (x, y) in which x represents longitudinal position along the waveguide and y represents transverse vibrations. If necessary we can let $y = (y_1, \dots, y_d)$ be multidimensional. In chemical applications, x might be a reaction coordinate with x large and negative corresponding to decoupled reactant molecules and x large and positive corresponding to decoupled product molecules (see Figure 1), while

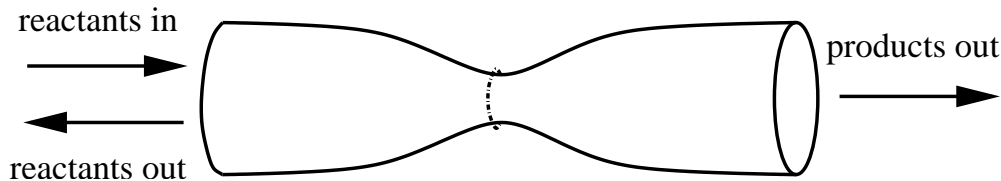


Figure 1. A schematic illustration is given of the waveguide problem considered in this paper, showing the case for an energy above threshold in which the transition state (part of which is indicated schematically by a dashed curve) separates reactants from products where the waveguide is at its narrowest. The surface shown is meant to illustrate a level surface in configuration space of the potential energy in the case of a three-degree-of-freedom Hamiltonian that is of the form kinetic-plus-potential (although no such explicit assumption regarding the form of the Hamiltonian is made in the calculation). Note that we use the term “waveguide” in a generalised sense in this paper to mean a Hamiltonian with a phase space bottleneck which asymptotes to a vibrational problem decoupled from free motion, and we do not deal explicitly with hard-wall or discontinuous potentials.

y describes internal vibrations of the reacting molecules. The quantum mechanics of this problem are described using a scattering matrix, which we write in the form

$$S(E) = \begin{pmatrix} r_{RR} & t_{RP} \\ t_{PR} & r_{PP} \end{pmatrix},$$

where, for example, the block t_{PR} maps asymptotic incoming states on the reacting side to the corresponding asymptotic outgoing states on the product side. In chemical jargon, t_{PR} gives state-selected reaction rates (labelled by the incoming mode number) together with the distribution of product states (labelled by the outgoing mode number). In this paper we will describe a semiclassical approximation for the operator

$$\hat{\mathcal{R}}(E) = t_{PR}^\dagger t_{PR}$$

which gives a probability of transmission for states incoming on the reactant side but which sums over outgoing states and does not give the distribution of product states. Although containing less information than the scattering matrix, this *reaction operator* has clear experimental relevance and, importantly in this context, admits semiclassical approximations which are considerably simpler. As described in detail in [8], this is because the orbits used in semiclassical approximation of $S(E)$ are singular near the boundary of the reacting subset of phase space whereas those used for $\hat{\mathcal{R}}(E)$ are not.

The reaction operator $\hat{\mathcal{R}}(E)$ has a clear relationship with the geometry of the classical transition state. It acts on the Hilbert space $\mathcal{H}_R^{\text{in}}$ of asymptotically propagating incoming states and the classical analogue of this space is a Poincaré section Σ_R^{in} obtained by fixing the reaction coordinate and the total energy E , for which (y, p_y) provide canonical coordinates. Let E be greater than threshold so that there is a nonempty reacting subset V of Σ_R^{in} — the boundary of V is the intersection with Σ_R^{in} of the stable

manifold of the NHIM. Then a phase space representation of $\hat{\mathcal{R}}(E)$ such as the Weyl symbol $\mathcal{W}_{\hat{\mathcal{R}}}(y, p_y)$ tends to the characteristic function of the reacting region V

$$\mathcal{W}_{\hat{\mathcal{R}}}(y, p_y) \sim \chi_V(y, p_y)$$

in the classical limit. Moreover, for finite values of \hbar , $\mathcal{W}_{\hat{\mathcal{R}}}(y, p_y)$ also incorporates quantum effects such as tunnelling, especially important outside V and near its boundary.

An explicit semiclassical approximation was presented for $\hat{\mathcal{R}}(E)$ in [8], of the form

$$\hat{\mathcal{R}}(E) = \frac{\hat{\mathcal{T}}(E)}{1 + \hat{\mathcal{T}}(E)}, \quad (1)$$

where the operator $\hat{\mathcal{T}}(E)$ is constructed from the linear stability properties of a complex periodic orbit. This complex periodic orbit has a real initial condition in the interior of V and returns to it after encircling the transition state region in a net imaginary time. The formula was derived by using a separable approximation of the Hamiltonian in the transition-state region to match waves propagating in the reactant and product channels. This separable approximation is valid only insofar as the transition state is small on classical scales and the result should therefore work only when the energy E is within $O(\hbar)$ of threshold, where the Liouville volume of V is $O(\hbar^d)$.

We will now show that, as long as the operator $\hat{\mathcal{T}}(E)$ is interpreted using fully nonlinear dynamics in a neighbourhood of the periodic orbit, Equation (1) is in fact valid over classical scales. The difference between the approach in [8] and the philosophy applied here has an analogy in the classical treatment of one-dimensional WKB solutions near turning points. The simplest way to treat turning points is to approximate the potential using a truncated Taylor expansion (linear for a single turning point and quadratic for two coalescing turning points) and to use the resulting solutions to match standard WKB approximations on either side. The method of comparison equations [9], on the other hand, seeks a change of variable which (up to higher-order corrections in \hbar) maps the potential more globally into a linear or quadratic form as required and this has the advantage of giving uniform results which apply over classical length scales. The approach in [8] is analogous to the method of truncating Taylor series whereas in this publication we pursue a transformation into normal form that is similar in spirit to the method of comparison equations.

The difference is that, for multidimensional problems, a deformation of configuration space variables alone as used in the method of comparison equations does not have sufficient range to put the problem in a solvable form and we must use transformations in phase space [10, 11, 12]. In this way a Hamiltonian which is a quantum analogue of the normal forms in [4] can be used and we arrive at a problem which, while not separable, is simple enough that scattering solutions can be written down. More importantly, the information we need to approximate $\hat{\mathcal{R}}(E)$ can be formulated in such a way that explicit reference to the normal form can be removed and the end result is a formula (of the same form as Equation (1)) which can be understood simply in terms of complex orbits starting and finishing on Σ_R^{in} .

We conclude this section with a brief overview of the paper. The essential features of the classical normal form are described in Section 2 and an overview is given of the corresponding quantum Hamiltonian. The normal form Hamiltonian is not separable but does have scattering solutions that are of separable form and these are described in Section 3. Because these scattering solutions do not fully separate in the eigenvalue equation and because the normal form Hamiltonian is not of kinetic-plus-potential type, using them to describe the transmission properties of a general scattering state is not straightforward. Nevertheless a simple solution to this problem is possible, which is outlined in Section 4. The final step in obtaining a usable result is to present the scattering solution in a basis-independent way, which we do in Section 5 in terms of quantised complex Poincaré mappings. Conclusions are presented in Section 6.

2. Classical and quantum normal forms

The basis for the calculation in this paper is a quantisation of the classical normal form for the Hamiltonian around an equilibrium. The classical normal form and its connection with classical transition state theory are described in detail in [4]. In this section we will describe the essential results and adapt some of the notation for our own purposes. We will then describe the important properties of a quantisation of this normal form.

2.1. The classical normal form

Let canonical coordinates $(q_0, p_0, q, p) = (q_0, p_0, q_1, \dots, q_d, p_1, \dots, p_d)$, be chosen so that the quadratic part of the Hamiltonian is

$$H(q_0, p_0, q, p) = \frac{\lambda}{2}(p_0^2 - q_0^2) + \sum_{i=1}^d \omega_i(q_i^2 + p_i^2) + \text{h.o.t.}$$

We denote by $f = 1 + d$ the number of degrees of freedom and we will refer to (q_0, p_0) as the reaction coordinates. In the context of collinear molecular collisions it is useful to let $q_0 = 0$ define a dividing surface between reactants and products with $q_0 < 0$ corresponding to reactants and $q_0 > 0$ corresponding to products. The reaction coordinates (q_0, p_0) are useful in interpreting the dynamics in this system, in which reaction amounts to crossing a parabolic potential barrier in that degree of freedom. It will also be useful for computational purposes however to allow alternative coordinates (Q, P) defined as a rotation of (q_0, p_0) so that

$$I = \frac{1}{2}(q_0^2 - p_0^2) = QP.$$

We will refer to I as the reaction action. It is positive for nonreacting trajectories, which are repelled by the parabolic barrier, and it is negative for the reacting trajectories, which cross over (see Figure 2).

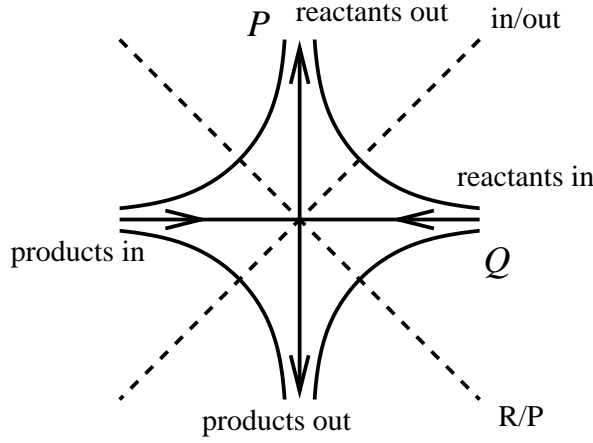


Figure 2. In classical phase space, we can identify in and out reactant and product channels with sectors in the QP -plane as illustrated in this figure. Orientations here are for $\partial H/\partial I < 0$. The dashed line labelled R/P divides reactants from products and the dashed line labelled in/out divides incoming from outgoing trajectories. For example, a point in phase space which projects to the sector in the QP -plane between dashed lines and containing the positive Q -axis is in the incoming reactant channel. The hyperbolae illustrate (projections of) typical trajectories evolving from the incoming to the outgoing channels. Note that in the classical picture dynamics is limited to an energetically allowed region bounded by hyperbolae in the second and fourth quadrants (assuming an energy above threshold), which is not illustrated here.

At higher order these canonical coordinates are defined so that the Hamiltonian depends on the reaction coordinates through the reaction action I only. To establish notation, we will write

$$H(Q, P, q, p) = H_{\text{rc}}(I) + H_{\text{ts}}(q, p, I) \quad (2)$$

where

$$H_{\text{ts}}(q, p, I) = H_0(q, p) + IH_1(q, p) + I^2H_2(q, p) + \dots$$

The leading parts of $H_{\text{rc}}(I)$ and $H_0(q, p)$ contain the quadratic truncation of the Hamiltonian shown above. That is

$$H_{\text{rc}}(I) = -\lambda I + \text{h.o.t.}$$

and

$$H_0(q, p) = \sum_{i=1}^d \omega_i(q_i^2 + p_i^2) + \text{h.o.t.}$$

We refer to $H_{\text{rc}}(I)$ and $H_{\text{ts}}(q, p, I)$ respectively as the reaction coordinate part and the transition-state part of the Hamiltonian, whence the subscripts.

We remark that for the following calculation to work, it is not necessary to put the transition-state part of the Hamiltonian in normal form. That is, the functions

$H_m(q, p)$ need not be written as functions of the transverse actions $J_i = (q_i^2 + p_i^2)/2$. This allows greater latitude in the normal form construction and might in principle alleviate problems with small denominators. We also remark that since we will be looking later at complex solutions to the equations of motion, there is an implicit assumption throughout this paper that the Hamiltonian is analytic in the transition state region.

2.2. The quantum normal form

The transformation to the classical normal form described above is achieved by making a canonical change of coordinates so that the Hamiltonian takes the desired form. The corresponding procedure in quantum mechanics is to use a unitary change of basis to the same effect. While a canonical transformation does not uniquely define a unitary operator in the quantum formalism, it is a well-established feature of the quantum-classical correspondence that such a connection can be achieved within semiclassical approximation. The connection was outlined by Miller in [10] using generating functions to write explicit approximations for corresponding unitary operators up to corrections of relative order $O(\hbar)$. Explicit and concrete rules describing how unitary transformations may be constructed which achieve normal form to higher order in \hbar have recently been published by Cargo et al in [11] and used there to derive compact higher-order Bohr-Sommerfeld rules. In the context of critical transmission, which is the application of interest here, transformation to quantum normal forms have been exploited by Colin de Verdière and Parisse in [12, 13, 14] to provide connection formulas describing the behaviour of wavefunctions near hyperbolic fixed points, and these have been used in [15] to calculate multidimensional quantisation rules which are valid near degenerate tori.

An alternative approach is to work directly with the quantum problem in making the transformation to normal form rather than simply quantising the classical normal form as we do here (see [16, 17, 18], for example). We do not adopt this viewpoint because we will in any case later need to employ semiclassically constructed nonperturbative unitary transformations to connect the normal form basis to the asymptotic basis used for the scattering matrix and there is no overall advantage in avoiding their use at this stage.

In this work we are interested only in constructing the quantum normal form to leading order semiclassically — that is, neglecting corrections of relative order $O(\hbar)$ in wavefunctions or terms of order $O(\hbar^2)$ in classical symbols. This is achieved using the “preliminary transformation” in the language of [11] and the resulting leading-order quantum normal form can be written straightforwardly as a direct copy of the classical normal form. A detailed discussion of this point would unnecessarily elongate the presentation here and will simply assert a direct equivalence (modulo higher order corrections) between quantum and classical Hamiltonians whenever necessary, referring the reader to [11, 12] for a proper explanation.

We therefore start, in analogy with (2), with a Hamiltonian of the form

$$\hat{H} = H_{\text{rc}}(\hat{I}) + H_{\text{ts}}(\hat{q}, \hat{p}, \hat{I}) \quad (3)$$

where \hat{I} and $H_{\text{ts}}(\hat{q}, \hat{p}, \hat{I})$ respectively denote quantisations of the classical symbols I and $H_{\text{ts}}(q, p, I)$. There are ordering issues in this correspondence, of course, but for the purposes of making semiclassical approximation to leading order in \hbar , it suffices to let \hat{I} and $H_{\text{ts}}(\hat{q}, \hat{p}, \hat{I})$ be Weyl quantisations. The key feature here is that \hat{I} and (\hat{q}, \hat{p}) act on different degrees of freedom and therefore commute. For concreteness, it may occasionally help to suppose that the transition-state part can be expanded in the form

$$H_{\text{ts}}(\hat{q}, \hat{p}, \hat{I}) = H_0(\hat{q}, \hat{p}) + \hat{I}H_1(\hat{q}, \hat{p}) + \hat{I}^2H_2(\hat{q}, \hat{p}) + \cdots \quad (4)$$

where we may in particular assume that

$$[\hat{I}, H_m(\hat{q}, \hat{p})] = 0.$$

The central result in this paper will be stated in an invariant way that does not refer explicitly to the normal form construction and the details of how this transformation is performed are not needed to use it. In addition, the essential idea of the calculation is understood simply on the basis of the normal form Hamiltonian itself. We will therefore simply quote the result and refer to Refs. [10, 11, 12] for detailed discussions of various approaches to making this transformation in practice.

3. Scattering solutions of the quantum normal form

Because higher-order terms in (4) couple the reaction degree of freedom to the transverse degrees of freedom, the normal form Hamiltonian is not separable in the simple-minded sense of the eigenvalue equation separating into a function of the reaction coordinate plus a function of the transition-state coordinates. Since the Hamiltonian depends on the reaction coordinate only through the reaction action I , however, it turns out that the eigenvalue equation nevertheless admits solutions which have a separable structure. We will use this property to reduce the transmission problem to one that is effectively one-dimensional and therefore solvable by standard techniques. Technical details of this reduction are given in the present section. In the next, it is shown how the results can be formulated in such a way that they no longer rely on an explicit consideration of the normal form.

3.1. The reaction coordinate part

The normal form construction provides us with a transformation to coordinates (Q, P) such that \hat{I} takes the form

$$\hat{I} = \frac{1}{2} (\hat{Q}\hat{P} + \hat{P}\hat{Q}), \quad (5)$$

which is the Weyl quantisation of QP . For interpretation of the results below in terms of conventional calculations, it may help to suppose that the reaction coordinate part \hat{H}_{rc}

of the total Hamiltonian acts on functions of a coordinate x (with conjugate momentum p_x) so that

$$\hat{I} = I(\hat{x}, \hat{p}_x) \quad (6)$$

and that the problem in the x -representation is close to a standard barrier-penetration problem. We could, for example, let (x, p_x) coincide with the coordinates (q_0, p_0) defined in Section 2.1 as a rotation of (Q, P) in the reaction-coordinate phase plane. In that case the transformation from (6) to (5) is achieved using a metaplectic rotation which rotates the phase plane clockwise through an angle $3\pi/4$ (to give Figure 2).

The operator \hat{I} has continuous spectrum and in x -representation we write the (improper) eigensolutions in the form

$$\hat{I}\psi_{\mathcal{I}}(x) = \mathcal{I}\psi_{\mathcal{I}}(x).$$

Then

$$E_{\text{rc}}(\mathcal{I}) = H_{\text{rc}}(I = \mathcal{I})$$

is the corresponding reaction-coordinate energy. These eigenfunctions are two-fold degenerate since we can send incoming waves from either the reactant or the product side of the barrier (see Appendix A). We will restrict our attention here to states which have an incoming component on the reactant side and outgoing components on both the reactant and product sides, but no incoming component on the product side, in which case there is a unique solution for each \mathcal{I} .

Either as an inverted parabolic barrier [9] or in the representation implied by (5) [12], the problem of finding eigensolutions of \hat{I} can be solved exactly and solutions of the scattering problem written in closed form. Details are given in Appendix A. For present purposes it is sufficient to note that there is a simple relationship describing the relative fluxes in the incoming and outgoing channels. Let the scattering state $\psi_{\mathcal{I}}(x)$ be normalised so that the incoming flux on the reactant side is normalised to unity (by construction, the incoming flux on the product side is zero). Then the outgoing fluxes on the reactant and product sides are, respectively,

$$T(\mathcal{I}) = \frac{1}{1 + e^{2\pi\mathcal{I}/\hbar}} \quad \text{and} \quad R(\mathcal{I}) = \frac{1}{1 + e^{-2\pi\mathcal{I}/\hbar}}. \quad (7)$$

In the barrier-penetration picture, $T(\mathcal{I})$ and $R(\mathcal{I})$ respectively represent probabilities of transmission and reflection. Note that by writing the transmission probability in the alternative form

$$T(\mathcal{I}) = \frac{e^{-2\pi\mathcal{I}/\hbar}}{1 + e^{-2\pi\mathcal{I}/\hbar}}$$

the unitarity condition

$$R(\mathcal{I}) + T(\mathcal{I}) = 1$$

becomes self-evident.

We make the following observations concerning this result.

- There is a symmetry between $R(\mathcal{I})$ and $T(\mathcal{I})$ on changing the sign of \mathcal{I} . This is to be expected on the basis of a phase-space portrait in (Q, P) coordinates (see Figure 2) in which changing the sign of \mathcal{I} simply exchanges reactants for products in the outgoing channels, but is less obvious in a barrier-penetration picture.
- The transmission and reflection coefficients do not change if we replace \hat{I} by a Hamiltonian $H(\hat{I})$ which is an arbitrary function of \hat{I} . This will be obvious after generalised fluxes are defined in the next section and a multidimensional version of this observation will be important in getting a simple formulation of the results in this paper.
- The expressions in (7) give semiclassical approximations to transmission and reflection coefficients for a generic potential barrier and can be derived from the standard representation of the Schrödinger equation using the method of comparison equations [9]. In the current calculation they are exact for any Hamiltonian which can be written as a function of the reaction action \hat{I} alone. However, there is in general semiclassical error arising from the transformation to normal form in the first place, during which terms of $O(\hbar^2)$ arise in the Hamiltonian which are neglected in the current analysis.

3.2. The transition state part

In the transverse degrees of freedom corresponding to (\hat{q}, \hat{p}) , we suppose a discrete spectrum parametrised by \mathcal{I} in the following way

$$H_{\text{ts}}(\hat{q}, \hat{p}, \mathcal{I})|\varphi_k(\mathcal{I})\rangle = E_{\text{ts}}^k(\mathcal{I})|\varphi_k(\mathcal{I})\rangle.$$

Here we suppose that a partial symbol $H_{\text{ts}}(\hat{q}, \hat{p}, \mathcal{I})$ is defined by replacing \hat{I} by its eigenvalue \mathcal{I} in $H_{\text{ts}}(\hat{q}, \hat{p}, \hat{I})$. If $H_{\text{ts}}(\hat{q}, \hat{p}, \hat{I})$ is given as a series of the form (4) then we can write, concretely,

$$H_{\text{ts}}(\hat{q}, \hat{p}, \mathcal{I}) = H_0(\hat{q}, \hat{p}) + \mathcal{I}H_1(\hat{q}, \hat{p}) + \mathcal{I}^2H_2(\hat{q}, \hat{p}) + \cdots.$$

In many interesting chemical applications, problems arise which have a Morse or Van der Waals type potential in the transverse degree of freedom for which the spectrum of $H_{\text{ts}}(\hat{q}, \hat{p}, \mathcal{I})$ is discrete at the bottom but becomes continuous above a threshold. We will confine ourselves, however, to energies at which asymptotically propagating scattering states correspond to reactant molecules in bound states, and for these cases the continuous spectrum (of \hat{H}_{ts}) does not participate. Rather than adjusting notation here to incorporate the continuous part of the spectrum we simply suppress it notationally and consider states labelled by the discrete index k only.

Results like those in [8] can be obtained by ignoring the \mathcal{I} -dependence of the states $|\varphi_k(\mathcal{I})\rangle$ and approximating them by $|\varphi_k(0)\rangle$ (or equivalently keeping only the leading part $H_0(\hat{q}, \hat{p})$ in the expansion above), but here we want to investigate the effect of coupling between the reaction and transverse degrees of freedom seen in the full

Hamiltonian. For a fixed \mathcal{I} we can assume that these states form an orthonormal set but note that we should assume in general that

$$\langle \varphi_{k'}(\mathcal{I}') | \varphi_k(\mathcal{I}) \rangle \neq \delta_{kk'} \quad (8)$$

if $\mathcal{I} \neq \mathcal{I}'$. This is the main point complicating the following analysis and means that we should be wary of assuming “obvious” results when describing issues of normalisation.

We will now describe how the discrete eigensolutions of the transverse problem combine with the scattering solutions found in the reaction-coordinate degree of freedom.

3.3. Eigenfunctions of the total Hamiltonian

With the conventions described in Sections 3.1 and 3.2,

$$|\Psi_{\mathcal{I},k}\rangle = \psi_{\mathcal{I}}(x) |\varphi_k(\mathcal{I})\rangle$$

are eigenstates of the full Hamiltonian \hat{H} in mixed position-bra-ket notation. These solutions satisfy

$$\hat{H} |\Psi_{\mathcal{I},k}\rangle = E_k(\mathcal{I}) |\Psi_{\mathcal{I},k}\rangle,$$

where

$$E_k(\mathcal{I}) = E_{\text{rc}}(\mathcal{I}) + E_{\text{ts}}^k(\mathcal{I}).$$

Note that the states $|\Psi_{\mathcal{I},k}\rangle$ are separable in form even though the Hamiltonian itself is not strictly speaking separable, as discussed at the beginning of this section. This nonseparability manifests itself through the dependence of the transverse eigenstates $|\varphi_k(\mathcal{I})\rangle$ on \mathcal{I} and in particular through the nonorthogonality condition (8).

Our aim is eventually to express results in such a way that explicit reference to the normal form transformation is unnecessary. For this purpose it is preferable to label states with the total energy instead of the reaction action, since the energy is defined independently of the representation used. For each value E of the total energy let, $\mathcal{I}_k(E)$ be defined implicitly as a solution of

$$E = E_k(\mathcal{I}).$$

Although we cannot write explicit expressions for $\mathcal{I}_k(E)$, we can suppose that in an energy range around threshold (where $E_{\text{rc}}(\mathcal{I}) = -\lambda\mathcal{I} + O(\mathcal{I}^2)$), these functions are well defined and single-valued for each k . We then define scattering states labelled by the total energy E and the mode number k as follows. Let

$$|\Psi_{E,k}\rangle = \psi_{\mathcal{I}_k(E)}(x) |\varphi_k(E)\rangle,$$

where for short we write

$$|\varphi_k(E)\rangle = |\varphi_k(\mathcal{I}_k(E))\rangle.$$

Note that in view of (8) we have

$$\langle \varphi_{k'}(E) | \varphi_k(E) \rangle \neq \delta_{kk'} \quad (9)$$

since on changing k the action eigenvalue $\mathcal{I} = \mathcal{I}_k(E)$ changes.

It is possible to normalise these states so that

$$\langle \Psi_{E',k'} | \Psi_{E,k} \rangle = \delta(E - E') \delta_{kk'}$$

in the usual way, but this convention turns out not to be particularly useful for our purposes and we will not apply it. Instead we will normalise these states so that they have unit flux in the incoming reaction channel. A discussion of normalisation by flux will also be necessary to appreciate how arbitrary scattering states may be constructed from these separated solutions, so we will defer further consideration of such issues until a method of flux calculation has been outlined in the next section.

4. Fluxes and sectional inner products

Since the normal-form Hamiltonian is not of kinetic-plus-potential type, we cannot use the usual definition of current

$$\mathbf{J} = \frac{\hbar}{2im} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*)$$

to calculate fluxes. There is a simple generalisation, however, which works for arbitrary Hamiltonians.

Let $\hat{\Theta}$ be a Hermitian operator which projects to one side of a section Σ which has codimension one in phase space. For example, if Σ is defined by fixing a configuration space coordinate then in position representation $\hat{\Theta}$ can represent multiplication by the characteristic function of a region which has boundary Σ . More generally, $\hat{\Theta}$ can be an operator for which a classical symbol such as the Weyl symbol rises from zero to unity in a classically small strip around Σ . Then the flux of a state $|\Psi\rangle$ across Σ is

$$F = \langle \Psi //_{\Sigma} \Psi \rangle, \tag{10}$$

where we define a sectional overlap by

$$\langle \Phi //_{\Sigma} \Psi \rangle = \frac{1}{i\hbar} \langle \Phi | [\hat{\Theta}, \hat{H}] | \Psi \rangle. \tag{11}$$

The notation here is adapted from [19] although a factor of $i\hbar$ has been introduced which will simplify matters later. Flux defined in this way is an integral part of transition-state calculations in the chemical literature (see [20, 21] for example) and similar ideas are used in [14, 22]. It is easily verified that if $\hat{\Theta}$ represents multiplication by the characteristic function of a region in configuration space then the flux reduces to the standard case of a surface integral of the current \mathbf{J} over the boundary. Although a flux calculation requires only the diagonal case in (11), it is useful to allow the nondiagonal case in the definition of sectional overlap. We will find in particular that the space of scattering solutions with a given total energy E can be identified with a quantised surface of section in one of the channels and the sectional overlap then provides a natural inner product for the corresponding Hilbert space.

4.1. Fluxes for the separated scattering states

We will now apply this generalised construction to compute fluxes in the normal form representation. Let the section Σ be chosen so that $\hat{\Theta}$ can be constructed in terms of the (\hat{Q}, \hat{P}) operators alone and commutes with \hat{q} and \hat{p} . In phase space this means that $\hat{\Theta}$ projects onto a region of phase space defined by a subset of the QP plane and independent of the (q, p) coordinates. Such a choice is natural if we view the complete system as a pinched waveguide (Figure 1) in which a section obtained by fixing reaction coordinates is used to define fluxes in and out of the reactant and product channels.

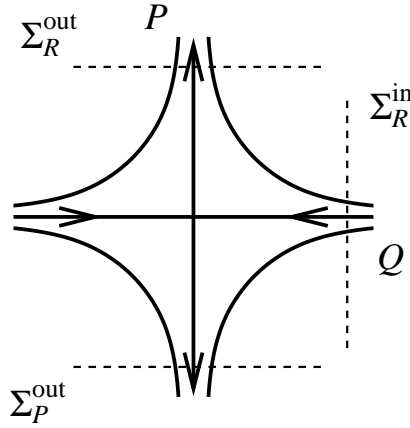


Figure 3. Sections which measure in and out fluxes in the product and reactant channels are illustrated schematically. Sections in full phase space are defined by fixing either the coordinate Q or the coordinate P appropriately in each case.

With the generalised definition of flux in (10) we are not, however, confined to fluxes across surfaces in configuration space and are free to define sections in phase space which distinguish incoming from outgoing flux in the reactant and product channels. For example, referring to Figure 3, a section Σ_R^{in} defined by a vertical line in the right-half of the QP -plane measures incoming flux in the reactant channel, whereas a horizontal line Σ_R^{out} in the upper half plane measures outgoing flux in the reactant channel and a horizontal line Σ_P^{out} in the lower half plane measures outgoing flux in the product channel. Fluxes across sections such as these corresponding to horizontal and vertical lines in the QP plane are especially easily computed in the QP representation. Details are given in Appendix A for the one-dimensional scattering solutions described in section 3.1 — here we simply note that relative fluxes are found to be of the form given in (7). Fluxes in the full system can be understood on the basis of these one-dimensional calculations in the following way.

By an abuse of notation, let us denote a one-dimensional flux for one of these reaction-coordinate sections by

$$\langle \psi_{\mathcal{I}} /_{\Sigma} \psi_{\mathcal{I}} \rangle = -\frac{1}{i\hbar} \langle \psi_{\mathcal{I}} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle. \quad (12)$$

Although we use similar notation to (10), it should be emphasised that this one-dimensional flux differs in having \hat{I} and not a Hamiltonian in the commutator and is not therefore a straightforward physical flux. There is also a minus sign, which compensates for the fact that $I(Q, P)$ generates a flow that is opposite in direction to the physical flow generated by the Hamiltonian — corresponding to $E'_k(\mathcal{I}) < 0$ in the discussion below. Although distinct from the physical flux, this quantity is prominent in the physical answer and the notation is useful for that reason.

We will see that in the full space the separated scattering states $|\Psi_{\mathcal{I},k}\rangle$ have sectional overlaps of the form

$$\langle \Psi_{\mathcal{I},k'} //_{\Sigma} \Psi_{\mathcal{I},k} \rangle = -E'_k(\mathcal{I}) \langle \psi_{\mathcal{I}} /_{\Sigma} \psi_{\mathcal{I}} \rangle \delta_{kk'}. \quad (13)$$

Alternatively, using states labelled by the total energy and normalised so that

$$|\tilde{\Psi}_{E,k}\rangle = \sqrt{-\mathcal{I}'_k(E)} |\Psi_{\mathcal{I}_k(E),k}\rangle, \quad (14)$$

we have

$$\langle \tilde{\Psi}_{E,k'} //_{\Sigma} \tilde{\Psi}_{E,k} \rangle = \langle \psi_{\mathcal{I}_k} /_{\Sigma} \psi_{\mathcal{I}_k} \rangle \delta_{kk'}. \quad (15)$$

The main point here is that the multidimensional scattering states have fluxes, and therefore probabilities of reflection and transmission, which reduce exactly to the one-dimensional case and we can apply (7) to scattering states of an arbitrary Hamiltonian in normal form. The transmission and reflection probabilities of the states $|\tilde{\Psi}_{E,k}\rangle$ can therefore be written

$$T_k(E) = \frac{1}{1 + e^{2\pi\mathcal{I}_k(E)/\hbar}} \quad \text{and} \quad R_k(E) = \frac{1}{1 + e^{-2\pi\mathcal{I}_k(E)/\hbar}} \quad (16)$$

and we can now use this as a basis with which to treat reactivity of an arbitrary stationary state.

We should emphasise that in view of the nonorthogonality of the transverse modes as expressed in (8) and (9), and in contrast to separable problems, these identities extending the one-dimensional results are not at all obvious. To prove them we consider separately the diagonal and nondiagonal cases, and treat them as follows.

Derivation of (13) in the diagonal case

We treat the diagonal case $k = k'$ first. Assume that \hat{H}_{ts} can be expanded in the form (4) and use

$$[\hat{\Theta}, \hat{I}^m] = [\hat{\Theta}, \hat{I}] \hat{I}^{m-1} + \hat{I} [\hat{\Theta}, \hat{I}] \hat{I}^{m-2} + \dots + \hat{I}^{m-1} [\hat{\Theta}, \hat{I}]$$

to deduce that

$$\langle \psi_{\mathcal{I}} | [\hat{\Theta}, \hat{I}^m] | \psi_{\mathcal{I}} \rangle = m \mathcal{I}^{m-1} \langle \psi_{\mathcal{I}} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle$$

and therefore that

$$\langle \Psi_{\mathcal{I},k} | [\hat{\Theta}, \hat{H}_{\text{ts}}] | \Psi_{\mathcal{I},k} \rangle = \sum_m m \mathcal{I}^{m-1} \langle \psi_{\mathcal{I}} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle \langle \varphi_k(\mathcal{I}) | H_m(\hat{q}, \hat{p}) | \varphi_k(\mathcal{I}) \rangle$$

$$\begin{aligned}
&= \langle \psi_{\mathcal{I}} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle \langle \varphi_k(\mathcal{I}) | \frac{\partial \hat{H}_{\text{ts}}(\hat{q}, \hat{p}, \mathcal{I})}{\partial \mathcal{I}} | \varphi_k(\mathcal{I}) \rangle \\
&= \langle \psi_{\mathcal{I}} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle \frac{\partial E_{\text{ts}}^k(\mathcal{I})}{\partial \mathcal{I}},
\end{aligned}$$

where in the last line we have invoked the Feynman-Hellman theorem. On adding a similar calculation for \hat{H}_{rc} we get the claimed result. The important feature is that the factor $E'_k(\mathcal{I})$ does not depend the choice of section across which to measure flux and relative fluxes reduce to the one-dimensional case.

Derivation of (13) in the nondiagonal case

To treat the nondiagonal case we use the identity

$$\begin{aligned}
\langle \psi_{\mathcal{I}'} | [\hat{\Theta}, \hat{I}^m] | \psi_{\mathcal{I}} \rangle &= \langle \psi_{\mathcal{I}'} | \left([\hat{\Theta}, \hat{I}] \hat{I}^{m-1} + \hat{I} [\hat{\Theta}, \hat{I}] \hat{I}^{m-2} + \dots \hat{I}^{m-1} [\hat{\Theta}, \hat{I}] \right) | \psi_{\mathcal{I}} \rangle \\
&= [\mathcal{I}^{m-1} + \mathcal{I}' \mathcal{I}^{m-2} + \dots \mathcal{I}'^{m-1}] \langle \psi'_{\mathcal{I}} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle \\
&= \frac{\mathcal{I}^m - \mathcal{I}'^m}{\mathcal{I} - \mathcal{I}'} \langle \psi'_{\mathcal{I}} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle
\end{aligned}$$

to deduce that

$$\langle \Psi_{\mathcal{I}',k'} | [\hat{\Theta}, \hat{I}^m \hat{H}_m] | \Psi_{\mathcal{I},k} \rangle = \langle \psi_{\mathcal{I}'} | [\hat{\Theta}, \hat{I}] | \psi_{\mathcal{I}} \rangle \langle \varphi_{k'}(\mathcal{I}') | \left[\frac{\mathcal{I}^m \hat{H}_m - \mathcal{I}'^m \hat{H}_m}{\mathcal{I} - \mathcal{I}'} \right] | \varphi_k(\mathcal{I}) \rangle.$$

On summing over m and doing a similar calculation for the reaction-coordinate part of the Hamiltonian we find that

$$\langle \Psi_{\mathcal{I}',k'} //_{\Sigma} \Psi_{\mathcal{I},k} \rangle = - \frac{E_k(\mathcal{I}) - E_{k'}(\mathcal{I}')}{\mathcal{I} - \mathcal{I}'} \langle \psi_{\mathcal{I}'} /_{\Sigma} \psi_{\mathcal{I}} \rangle \langle \varphi_{k'}(\mathcal{I}') | \varphi_k(\mathcal{I}) \rangle.$$

In terms of the energy-labelled states $|\Psi_{E,k}\rangle = |\Psi_{\mathcal{I}_k(E),k}\rangle$, we have

$$\langle \Psi_{E',k'} //_{\Sigma} \Psi_{E,k} \rangle = - \frac{E - E'}{\mathcal{I}_k(E) - \mathcal{I}_{k'}(E')} \langle \psi_{\mathcal{I}_{k'}(E')} /_{\Sigma} \psi_{\mathcal{I}_k(E)} \rangle \langle \varphi_{k'}(E') | \varphi_k(E) \rangle.$$

These sectional overlaps vanish as E' approaches E unless $k = k'$, in which case we recover the diagonal result. This completes the derivation of (13).

4.2. Fluxes for general scattering states and reduced Hilbert space

Let $\mathcal{H}_R^{\text{in}}$ denote the subspace of scattering states of a fixed total energy E which are incoming on the reactant side and have no incoming flux on the product side. In the applications we consider the scattering problem will asymptote to a waveguide-type problem in which there are a finite number M of propagating channels (corresponding to the energetically accessible bound states of the reacting molecules) and the space $\mathcal{H}_R^{\text{in}}$ will therefore be finite-dimensional. We assert that the space $\mathcal{H}_R^{\text{in}}$ is in fact essentially a quantisation of a classical surface of section (in the incoming reactant channel) in the sense of Bogomolny [23], with the inner product being given by sectional overlaps of the form in (11).

Let us write a general asymptotically-propagating scattering state in the form

$$|\Phi\rangle = \sum_{k=1}^M a_k \frac{|\tilde{\Psi}_{E,k}\rangle}{\sqrt{\langle\psi_{\mathcal{I}_k} / \Sigma_R^{\text{in}} \psi_{\mathcal{I}_k}\rangle}}. \quad (17)$$

Then the total incoming flux for this state is

$$F_R^{\text{in}} = \langle\Phi // \Sigma_R^{\text{in}} \Phi\rangle = \sum_{k=1}^M |a_k|^2$$

while in view of (15) and (16) the outgoing flux in the reactant channel is

$$F_R^{\text{out}} = \langle\Phi // \Sigma_R^{\text{out}} \Phi\rangle = \sum_{k=1}^M \frac{1}{1 + e^{2\pi\mathcal{I}_k(E)/\hbar}} |a_k|^2$$

and the outgoing flux in the product channel is

$$F_P^{\text{out}} = \langle\Phi // \Sigma_P^{\text{out}} \Phi\rangle = \sum_{k=1}^M \frac{1}{1 + e^{-2\pi\mathcal{I}_k(E)/\hbar}} |a_k|^2.$$

Furthermore, between any two such scattering states the sectional overlap

$$\langle\Phi' // \Sigma_R^{\text{in}} \Phi\rangle = \sum_{k=1}^M a_k'^* a_k$$

provides a natural inner product for $\mathcal{H}_R^{\text{in}}$.

We can regard $\mathcal{H}_R^{\text{in}}$ abstractly as a space spanned by an orthonormal basis $\{|k\rangle\}_{k=1}^M$ whose elements

$$|k\rangle \sim \frac{|\tilde{\Psi}_{E,k}\rangle}{\sqrt{\langle\psi_{\mathcal{I}_k} / \Sigma_R \psi_{\mathcal{I}_k}\rangle}}$$

are in one-to-one correspondence with the scattering states $|\tilde{\Psi}_{E,k}\rangle$, normalised to have unit incoming flux. A general element

$$|\varphi\rangle = \sum_{k=1}^M a_k |k\rangle$$

of this reduced space can be extended to a scattering state of the form given in (17) for which the total energy is fixed but which is not necessarily an eigenstate of the transverse Hamiltonian \hat{H}_{ts} . The inner product between two reduced states can be defined through sectional overlaps

$$\langle\varphi'|\varphi\rangle = \langle\Phi' // \Sigma_R \Phi\rangle$$

of the corresponding extended states.

The benefit of this abstraction is that we can compute outgoing fluxes in the product channel using matrix elements

$$F_P^{\text{out}} = \langle\varphi|\hat{\mathcal{R}}(E)|\varphi\rangle \quad (18)$$

of a reaction operator

$$\hat{\mathcal{R}}(E) = \sum_{k=1}^M \frac{|k\rangle\langle k|}{1 + e^{2\pi\mathcal{I}_k(E)/\hbar}} = \sum_{k=1}^M \frac{e^{-2\pi\mathcal{I}_k(E)/\hbar}}{1 + e^{-2\pi\mathcal{I}_k(E)/\hbar}} |k\rangle\langle k| \quad (19)$$

which is diagonal in this basis. By writing the outgoing flux as a matrix element of an operator defined on $\mathcal{H}_R^{\text{in}}$ we have in large part achieved the goal of this paper, which is to generalise the construction in [8] so that there is no longer a restriction to states supported in a classically small region of phase space. In fact, the only restriction on incoming states here is that they should be supported in the region of phase space where the normal form in (2) provides an accurate description of dynamics. Although undoubtedly a restricted subset of phase space, this domain has classical dimensions.

The current version is tied to the normal form, however and in order for this operator to be of any practical use, we really need a way of constructing it which does not call on us explicitly to construct the normal form or the basis vectors $|k\rangle$. As a start in this direction, note that if we denote

$$\hat{\mathcal{T}}(E) = \sum_k e^{-2\pi\mathcal{I}_k(E)/\hbar} |k\rangle\langle k|, \quad (20)$$

then $\hat{\mathcal{R}}(E)$ can be written in the form (1) promised in the introduction. This is precisely the form given in [8], where $\hat{\mathcal{T}}(E)$ was a *tunnelling operator* defined as a quantised surface of section map in the neighbourhood of a complex periodic orbit. We will show in the Section 5 that the same interpretation can be imposed on $\hat{\mathcal{T}}(E)$ in the present case with the difference that, unlike in [8], restriction to a neighbourhood of the periodic orbit small enough for linearised dynamics to be used is no longer necessary.

4.3. The microcanonical cumulative reaction probability

The trace

$$N(E) = \text{Tr } \hat{\mathcal{R}}(E) = \sum_{k=1}^M \frac{1}{1 + e^{2\pi\mathcal{I}_k(E)/\hbar}} \quad (21)$$

of the reaction operator is the so-called microcanonical cumulative reaction probability. Results for $N(E)$ equivalent to those that would be obtained by using linearised dynamics in $\hat{\mathcal{R}}(E)$ in the manner of [8] were obtained by Miller in [24]. Semiclassical approximations for $N(E)$ have also been given in [20, 25] which include nonlinear effects in the transition state degrees of freedom by using expansions in the transition-state quantum numbers (a related treatment of tunnelling using normal-form coordinates has been given in [26]). A thermalised version has been given in [27] and see [28] for a semiquantum calculation. A discussion emphasising the fluctuations that occur in $N(E)$ as the summands in (21) switch on with increasing E can be found in [29, 30]. We also remark that a discussion of $N(E)$ has recently been given in [6] which uses the same language of normal forms that we use here.

The major benefit of the current work is that, once a prescription has been given in the next section for computing $\hat{\mathcal{R}}(E)$ without recourse to the normal form, we will have

an explicit prescription for distributing the total reaction probability in $N(E)$ among incoming states or, equivalently, using the Wigner-Weyl formalism, for understanding how the reaction probability is distributed in phase space. In principle, this calculation can be implemented simply by computing complex trajectories near the complex periodic orbit used in [8] and does not require a particular deconstruction of the Hamiltonian such as provided by a normal form (although normal forms do help in inverting the operator $1 + \hat{T}(E)$ in (1) as we will discuss).

5. Getting away from the normal form

Equation (1) promises the ability to treat reaction problems without having to deal explicitly with the normal form and separated stationary states. In this section we show how this can be done by interpreting $\hat{T}(E)$ as a tunnelling operator in the sense of [8, 19] which can be understood independently of the normal form construction.

5.1. The complex return map in normal form coordinates

We first describe how a complex return map is expressed in terms of normal form coordinates. Let (I, θ) be action angle variables in the QP plane such that in the positive quadrant

$$\begin{aligned} Q &= \sqrt{I}e^\theta \\ P &= \sqrt{I}e^{-\theta}. \end{aligned}$$

We have $I = QP$, consistent with previous notation. Although the system is hyperbolic and not normally associated with periodic motion, there is in fact an imaginary period, expressed by the identities

$$\begin{aligned} Q(\theta + 2\pi i) &= Q(\theta) \\ P(\theta + 2\pi i) &= P(\theta). \end{aligned}$$

In other words, the Hamiltonian flow generated by I in the complexified QP plane has period $2\pi i$. We will now show that an extension of this periodic flow to the full system can be used to define a complex Poincaré return map and that this map has a fixed point corresponding to a complex periodic orbit.

Let us restrict initial conditions to a surface of section Σ_R^{in} defined by fixing Q as in Figure 3, along with the total energy E , and let the condition

$$E = H(q, p, I) \tag{22}$$

implicitly define the function $h(q, p, E)$ on Σ_R^{in} by

$$I = h(q, p, E) - e(E).$$

Here we regard (q, p) as canonical coordinates for Σ_R^{in} and $e(E)$ is defined so that the minimum of $h(q, p, E)$ on Σ_R^{in} is zero, as described more explicitly below. Differentiating (22) with respect to the transverse coordinates q and p while keeping E fixed gives

$$0 = \frac{\partial H}{\partial I} \nabla h + \nabla H,$$

which in turn gives

$$X_h = -\frac{1}{\dot{\theta}} \tilde{X}_H = - \left(\begin{array}{c} \frac{dq}{d\theta} \\ \frac{dp}{d\theta} \end{array} \right),$$

where \tilde{X}_H denotes the projection of the full flow vector X_H defined by H onto the transverse degrees of freedom (q, p) and we have used $\dot{\theta} = \partial H / \partial I$. The flow defined by X_h can therefore be regarded as a restriction to the (q, p) degrees of freedom of the full flow, reparametrised so that time t is replaced with the angle variable θ .

Letting θ evolve from 0 to the final value $2\pi i$, trajectories are described in full phase space which start on Σ_R^{in} and return to it — recall that the (Q, P) coordinates which are used to define Σ_R^{in} are periodic under this evolution. Integrating the flow vector $-X_h$ for a time $2\pi i$ then generates a complex symplectic map

$$\mathcal{F} : \Sigma_R^{\text{in}} \rightarrow \Sigma_R^{\text{in}}$$

which we can denote by

$$\mathcal{F} = \exp[-2\pi i X_h] \tag{23}$$

in Lie-algebraic notation. This is precisely the classical map used to construct the tunnelling operator in [8].

Before describing explicitly how the quantisation works, it is helpful to see how the complex periodic orbit which provides a fixed point of \mathcal{F} arises in normal form coordinates. By construction, the quadratic part of the Hamiltonian $H(q, p, I)$ is elliptic in the transverse degrees of freedom. As a result, the sectional Hamiltonian $h(q, p, E)$ has a minimum $(q_e(I), p_e(I))$, for sufficiently small I at least, for which

$$\nabla h(q_e(I), p_e(I), E) = 0$$

and which coincides with the origin of Σ_R^{in} in the threshold case $I = 0$. We define $e(E)$ above so that $h(q_e, p_e, E) = 0$ and a Taylor expansion of $h(q, p, E)$ about $(q_e(I), p_e(I))$ begins with quadratic terms. This minimum is an equilibrium of the flow defined by X_h on Σ_R^{in} and is therefore a fixed point of \mathcal{F} . In full phase space, the trajectory starting with coordinates $(q_e(I), p_e(I))$ on Σ_R^{in} evolves so that the coordinates I and (q, p) are fixed and defines a periodic orbit as θ evolves from 0 to $2\pi i$. The time period corresponding to this evolution is $-i\tau(E)$ where

$$\tau = -\frac{2\pi}{\dot{\theta}} = -\frac{2\pi}{\partial H(q_e, p_e, I) / \partial I} = 2\pi e'(E).$$

and its action is an imaginary number $S(E) = iK_0(E)$ where

$$K_0 = \frac{1}{i} \oint I d\theta = 2\pi I = -2\pi e(E).$$

In [8] a linearisation of dynamics about this complex periodic orbit was used to approximate $\hat{\mathcal{R}}(E)$ which here corresponds to truncating a Taylor series of $h(q, p, E)$ about $(q_e(I), p_e(I))$ at quadratic order. The essential conclusion of this paper is that a complete description of the reaction operator can be achieved simply by replacing this truncation with the full sectional Hamiltonian $h(q, p, E)$.

5.2. The tunnelling operator

The tunnelling operator is defined to be a quantisation of the classical map \mathcal{F} [8, 19]. Using (23) we can write concretely,

$$\hat{\mathcal{T}} = e^{2\pi(e-\hat{h})/\hbar},$$

where $\hat{h} - e$ is the restriction of the operator \hat{I} to the quantum analogue $\mathcal{H}_R^{\text{in}}$ of Σ_R^{in} defined in the Section 4. In that case

$$(\hat{h} - e)|k\rangle = \mathcal{I}_k(E)|k\rangle$$

and

$$e^{2\pi(e-\hat{h})/\hbar}|k\rangle = e^{-2\pi\mathcal{I}_k(E)/\hbar}|k\rangle$$

and the identification in the previous section of $\hat{\mathcal{T}}(E)$ in (20) as a tunnelling operator is confirmed.

It should be emphasised that while the sectional Hamiltonian h was used in making this identification, it is not necessary to construct it explicitly, or even to refer to it, in order to construct the map \mathcal{F} and to approximate its quantum analogue $\hat{\mathcal{T}}(E)$ semiclassically. The map \mathcal{F} can be constructed simply by integrating orbits as described in references [8, 19]. From the dynamical characteristics of these orbits, Van Vleck-type approximations for $\hat{\mathcal{T}}(E)$ can be written as described in [23], for example. Alternatively, the Weyl symbol of $\hat{\mathcal{T}}(E)$ can be obtained as described in [31]. Coherent state representations are also possible ([32, 33] and references therein). In all of these approaches the dynamical information needed is naturally provided as a result of the orbit computation and $h(q, p)$ is not needed explicitly.

We note finally that while it would be quite easy to write a version of (19) that describes the full scattering matrix in the normal form representation, so that we could determine the distribution of product states for each reactant state, it is less obvious how the normal form result could be interpreted in a basis-independent way in that case. Any such reformulation would have to take into account the fact that orbits contributing to the scattering matrix itself [10] depend singularly on initial conditions near the reacting boundary. The simplicity of the normal form representation suggests, however that such a uniformisation might be feasible, although we do not pursue it here.

5.3. Asymptotic basis for the reaction operator

Although the reaction operator is diagonal with respect to the stationary states $|\tilde{\Psi}_{E,k}\rangle$ computed in terms of the normal form, it will not in general be diagonal in the basis of asymptotically decoupled stationary states that is used to write the scattering matrix. In fact, since the normal form will in general only provide an accurate description of dynamics in a neighbourhood of the transition state, we need an independent method to describe how these states can be extended to the asymptotic regions of the reactant channel and the operator $\hat{\mathcal{R}}(E)$ written in the standard asymptotic basis.

To achieve this we note simply that once the transmission problem has been solved locally in the transition state region, the solution can be extended to the asymptotic region by applying quantised surface-of-section maps, such as described in [23], for example. Once outside the transition state region, these mappings can be constructed on the basis of primitive semiclassical approximations and amount in the classical picture simply to conjugating the complex Poincaré map \mathcal{F} with standard real ones. As when transforming to the quantum normal form in the first place, the end result of this process is easily stated and the details omitted in the interests of brevity since they follow discussions elsewhere [23].

To be more specific about this conjugation, let the coordinates (x, y, p_x, p_y) be as described in the introduction and let the Hamiltonian decouple asymptotically in the reactant channel according to

$$H(x, y, p_x, p_y) \simeq H_{\text{asympt}}(y, p_y) + H_{\text{tr}}(x, p_x). \quad (24)$$

Here $H_{\text{asympt}}(y, p_y)$ describes the internal vibrational motion of the reacting molecules and $H_{\text{tr}}(x, p_x)$ is a kinetic energy term for the relative motion of centres of mass. In the simplest atom-diatom collinear case we might have

$$H_{\text{tr}}(x, p_x) = \frac{p_x^2}{2M}$$

where M is the atom-diatom relative mass and

$$H_{\text{asympt}}(y, p_y) = \frac{p_y^2}{2m} + V_{\text{AB}}(y)$$

where m is the diatomic relative mass and $V_{\text{AB}}(q)$ the diatomic interaction potential.

The separated asymptotic solutions are denoted

$$|\Phi_{n,E}\rangle = \chi_{E,n}(x)|\psi_n\rangle$$

where $\chi_{E,n}(x)$ is a plane-wave eigenfunction of \hat{H}_{tr} with energy $E - E_n$ and normalised to have unit incoming flux while $|\psi_n\rangle$ is an eigenstate of internal dynamics with energy E_n . There is a phase convention implicit in writing the scattering matrix, which in the present case amounts to specifying the phase of $\chi_{E,n}(x)$. In the standard plane-wave case

$$\chi_{E,n}(x) = \frac{e^{ik_n x}}{\sqrt{v_n}},$$

where $v_n = \hbar k_n$ ensures unit incoming flux, we can understand the phase of $\chi_{E,n}(x)$ as being fixed at $x = 0$.

The phase convention in the asymptotic regime is then obtained by extending the complete scattering state $|\Phi_{n,E}\rangle$ from a section Σ_R^0 defined by $x = 0$ to a section Σ_R^{asympt} defined by a large and negative value of x . This extension is affected in the semiclassical scheme [23] by quantising a surface of section mapping

$$\mathcal{F}_0 : \Sigma_R^0 \rightarrow \Sigma_R^{\text{asympt}}$$

constructed using the uncoupled dynamics of the Hamiltonian in (24) — since the plane wave is travelling to the right, this will be achieved in negative time. Scattering of the

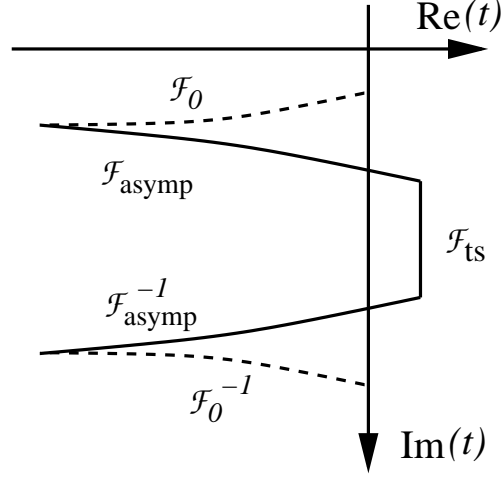


Figure 4. The path in the complex time plane which achieves the conjugation (25) is illustrated schematically. The dashed lines indicate evolution under decoupled dynamics. For the complex periodic orbit defining a fixed point of \mathcal{F} , the contour segments corresponding to \mathcal{F}_0 , $\mathcal{F}_{\text{asyp}}$ and their inverses are parallel to the real axis, while the segment for \mathcal{F}_{ts} is parallel to the imaginary axis. The time evolution of each segment develops both real and imaginary parts as the initial condition moves away from this fixed point.

resulting incoming state then proceeds by first mapping from the section Σ_R^{asyp} to a section Σ_R^{ts} near the transition state using the fully coupled dynamics,

$$\mathcal{F}_{\text{asyp}} : \Sigma_R^{\text{asyp}} \rightarrow \Sigma_R^{\text{ts}}.$$

If Σ_R^{ts} is in the domain of the normal form then its transmission probability is understood using a complex return map

$$\mathcal{F}_{\text{ts}} : \Sigma_R^{\text{ts}} \rightarrow \Sigma_R^{\text{ts}}$$

of the kind described in Section 5.1. Finally, we complete the transformation to the asymptotic basis by mapping back to the asymptotic section Σ_R^{asyp} using the inverse $\mathcal{F}_{\text{asyp}}^{-1}$ of $\mathcal{F}_{\text{asyp}}$ and then mapping to Σ_R^0 using the inverse \mathcal{F}_0^{-1} . The end result is a map

$$\mathcal{F} = \mathcal{F}_0^{-1} \mathcal{F}_{\text{asyp}}^{-1} \mathcal{F}_{\text{ts}} \mathcal{F}_{\text{asyp}} \mathcal{F}_0 \quad (25)$$

which is conjugate to \mathcal{F}_{ts} but which is adapted to the phase convention used for the scattering matrix. A quantisation of this map gives a tunnelling operator $\hat{T}(E)$ appropriate to the asymptotic basis defined by the states $|\Phi_{n,E}\rangle$.

Note that by conjugating \mathcal{F}_{ts} by $\mathcal{F}_{\text{asyp}}$, we can extend the return map far beyond the domain where the normal form applies. The outer conjugation by \mathcal{F}_0 is not strictly necessary to calculate reaction probabilities of incoming states $|\Phi_{n,E}\rangle$ since the transverse parts $|\psi_n\rangle$ are eigenfunctions of the quantisation of \mathcal{F}_0 and the resulting eigenphases cancel in the transformed version

$$F_P^{\text{out}} = \langle \psi_n | \hat{\mathcal{R}}(E) | \psi_n \rangle$$

of (18). However phases are important for cross terms if we want to treat general scattering states

$$|\Phi\rangle = \sum_{n=1}^M c_n |\Phi_{n,E}\rangle$$

and they are also important for representations of $\hat{\mathcal{R}}(E)$ in phase space. We also remark that $\mathcal{F}_{\text{asympt}}$ will not in general commute with \mathcal{F}_{ts} and the reaction operator will therefore *not* be diagonal in the asymptotic basis defined by the states $|\Phi_{n,E}\rangle$. On noting that the conjugation in (25) amounts simply to a change of representation so that Σ_R^0 can be identified with the section Σ_R^{in} , however, we see that the tunnelling operator written in this basis is not fundamentally different from the one described in Section 5.2.

Finally, we note that the conjugation in (25) is particular to a waveguide problem in which the plane wave part is written in terms of a coordinate x with phases fixed at $x = 0$. If different conventions are used for the asymptotic coordinates or for the part $\chi_{E,n}(x)$ of the scattering state, then the part \mathcal{F}_0 of the conjugation must be redefined accordingly.

5.4. Limitations of the derivation

No approximations are made in getting to the reaction-operator form of the outgoing flux in (18) and (19) once the quantum normal form of the Hamiltonian in (3) is written down. The sources of error are in transforming to the quantum normal form in the first place and in transforming to the asymptotic scattering basis after the reaction operator has been found in the normal form representation (18) and (19). We now comment on some of the issues affecting this approach.

The classical normal form is a formal series which describes the dynamics locally in a neighbourhood of the transition state region. It is clear that writing a quantum version of it as we do here is a formal step which will ultimately require a more careful justification. Issues of convergence become especially important if we pursue the limit $\hbar \rightarrow 0$ in its literal sense and we have not addressed such questions here. From a purely practical point of view, however, if one's aim is to achieve an approximation that works well for a small but fixed value of \hbar , then it suffices to describe the dynamics to a corresponding level of accuracy in phase space and the normal form is certainly capable of that in the sorts of parameter regimes that arise in chemical applications [34].

Results of a numerical investigation are outlined in [34] which indicate that the expression in (1) works very well when $\hat{\mathcal{T}}(E)$ is computed directly from the complex orbits of the Poincaré return map \mathcal{F} . We also note that since (1) can be interpreted theoretically without reference to the normal form, it seems natural to expect that it applies independently of the normal form itself. We therefore conjecture that, despite the limitations of the derivation presented here, Equation (1) is in fact “classically exact” in the sense that no errors arise from classical dynamics side of the calculation once $\hat{\mathcal{T}}(E)$ is interpreted as the quantisation of \mathcal{F} and the only approximation is the usual semiclassical one which vanishes as $\hbar \rightarrow 0$.

It is important to add the qualification, however, that even if the conjecture is correct, there are good reasons to expect it to apply only locally, at least in the simple form described in sections 5.1 and 5.2. The return map \mathcal{F} describes a unique image for initial conditions in a neighbourhood of the complex periodic orbit and for energies sufficiently close to threshold. In practical terms, this means there is a unique complex solution satisfying the boundary conditions required of orbits by semiclassical approximation of $\hat{T}(E)$ in the usual representations [8, 34]. Sufficiently far away, however, bifurcations are likely to occur where this structure breaks down and these are not described by the current formulation. In fact, it has been shown in [35] (and see [36, 37, 38, 39] for related work) that complex orbits contributing to the scattering matrix can be chaotic and are subject to intricate pruning by the Stokes' phenomenon, while numerical evidence [34] suggests that the same is true of the orbits contributing to $\hat{T}(E)$ sufficiently far from the centre of the reacting region. At an even more basic level, the NHIM itself may undergo bifurcation once the energy rises far enough above threshold and in this case the whole bottleneck picture at the basis of our calculation is no longer correct. Global recrossing may occur and resonances arise in the quantum mechanics which are not described by the simple picture of transmission probability we have here. It should be stressed, however, that whatever the limits are on the domain where contributing dynamics are simple, they are independent of \hbar and therefore have classical scales.

Finally, we remark that even though the tunnelling operator $\hat{T}(E)$ can be routinely approximated using semiclassical approximations, the inverse of $1 + \hat{T}(E)$ that occurs in (1) is more problematic. Closed form analytic approximations are possible if we know the sectional Hamiltonian $h(q, p)$ (see [8] for the harmonic case) but more work is needed to provide an approximation that works directly in terms of the map \mathcal{F} .

6. Conclusion

We have characterised the semiclassical transmission of waves across a phase-space bottleneck using a reaction operator constructed from a complex Poincaré mapping. In contrast to previous work [8], this construction is not restricted to energies and parts of phase space in a classically small neighbourhood of the transition state at threshold.

A phase-space representation of the reaction operator will be largely supported in the classically reacting subset of phase space, but will also incorporate tunnelling and other quantum effects at the boundary of this region, where trajectories approach the NHIM along its stable manifold. The only dynamical information needed to apply the approximation described in this paper is contained in the complex Poincaré mapping and explicit consideration of normal forms, or other special assumptions regarding the dynamics such separability or adiabatic approximation, are unnecessary. We also note that the particular trajectories used to define this map are well behaved at the reacting boundary. Therefore, despite the fact that the fate of trajectories changes discontinuously across the reacting boundary, the result here uniformly describes the

transition from classically allowed transmission inside the reacting region to reaction entirely by tunnelling outside it.

We conclude by noting that in its current form the result here is restricted to collinear problems. In order for the approach to be used in completely realistic models, the marginally stable degrees of freedom associated with rotational symmetry will need to be incorporated. This aspect needs further investigation.

Acknowledgements

This work was supported the European Network MASIE.

Appendix A. Scattering for the one-dimensional normal form

The one-dimensional problem is especially easily solved in a representation in which the reaction action operator takes the form (5) and \hat{P} acts on functions of Q according to

$$\hat{P}\psi(Q) = \frac{\hbar}{i}\psi'(Q).$$

In this case the eigenvalue equation $\hat{I}\psi = \mathcal{I}\psi$ is a first order differential equation

$$\frac{\hbar}{i} \left(Q \frac{d}{dQ} + \frac{1}{2} \right) \psi(Q) = \mathcal{I}\psi(Q) \quad (\text{A.1})$$

and this can be solved in elementary terms without the complication of parabolic cylinder functions that arise in the conventional representation of an inverted oscillator [9]. This approach has in particular been exploited in [12] to treat scattering in one-dimensional networks of tori and we refer to that publication for more detail of the following calculation. It is useful, however, to reiterate some of the main points here and to emphasise flux calculations, which form a basis for the discussion in the main text.

The eigenvalue equation (A.1) leads to doubly degenerate eigenfunctions $\psi_{\mathcal{I}}^{\pm}(Q)$ of the forms

$$\psi_{\mathcal{I}}^{+}(Q) = \Theta(Q)Q^{-1/2+i\mathcal{I}/\hbar}$$

and

$$\psi_{\mathcal{I}}^{-}(Q) = \psi_{\mathcal{I}}^{+}(-Q)$$

respectively. We will concentrate on the solution $\psi_{\mathcal{I}}^{+}(Q)$, which as we will now show represents bombardment of the equilibrium from the reactant side and is therefore the solution singled out in section 3.1.

The incoming flux is normalised as follows. Let the projection operator $\hat{\Theta}$ have the Q -representation

$$\hat{\Theta}\psi(Q) = \Theta(Q_0 - Q)\psi(Q)$$

so that it measures flux from right to left in the QP -plane across a section Σ_R defined by $Q = Q_0$. Then

$$\frac{1}{i\hbar}[\hat{\Theta}, \hat{I}] = \frac{1}{2i\hbar} \left(\hat{Q}[\hat{\Theta}, \hat{P}] + [\hat{\Theta}, \hat{P}]\hat{Q} \right) = -Q\delta(Q - Q_0)$$

and sectional overlaps are of the form

$$\langle \psi /_{\Sigma_R} \psi \rangle = -\frac{1}{i\hbar} \langle \psi | [\hat{\Theta}, \hat{I}] | \psi \rangle = Q_0 |\psi(Q_0)|^2.$$

The case $Q_0 > 0$ corresponds to incoming flux on the reactant side. We then denote $\Sigma_R = \Sigma_R^{\text{in}}$ and get

$$\langle \psi_{\mathcal{I}}^+ /_{\Sigma_R^{\text{in}}} \psi_{\mathcal{I}}^+ \rangle = Q_0 |Q_0^{-1/2+i\mathcal{I}/\hbar}|^2 = 1.$$

A section with $Q_0 < 0$ gives a flux in the incoming product channel and this vanishes for the state $\psi_{\mathcal{I}}^+(Q)$, consistent with our interpretation of it as an incoming state in the reactant channel.

Outgoing fluxes are naturally measured in momentum representation

$$\varphi(P) = \langle P | \psi \rangle$$

using projections of the form

$$\hat{\Theta}\varphi(P) = \Theta(P - P_0)\varphi(P).$$

In this representation we have

$$\frac{1}{i\hbar}[\hat{\Theta}, \hat{I}] = \frac{1}{2i\hbar} \left([\hat{\Theta}, \hat{Q}]\hat{P} + \hat{P}[\hat{\Theta}, \hat{Q}] \right) = -P\delta(P - P_0)$$

and therefore

$$\langle \psi /_{\Sigma_P} \psi \rangle = P_0 |\varphi(P_0)|^2.$$

To complete the calculation we therefore need to evaluate

$$\begin{aligned} \varphi_{\mathcal{I}}^+(P) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-iQP/\hbar} \psi_{\mathcal{I}}^+(Q) dQ \\ &= \frac{1}{\sqrt{2\pi\hbar}} \left(\frac{|P|}{\hbar} \right)^{-1/2-i\mathcal{I}/\hbar} \int_0^{\infty} e^{-i\sigma q} q^{-1/2+i\mathcal{I}/\hbar} dq \\ &= \frac{\hbar^{i\mathcal{I}/\hbar}}{\sqrt{2\pi}} e^{-i\sigma\pi/4+\sigma\pi\mathcal{I}/(2\hbar)} \Gamma\left(\frac{1}{2} + \frac{i\mathcal{I}}{\hbar}\right) |P|^{-1/2-i\mathcal{I}/\hbar}, \end{aligned}$$

where σ is the sign of P . Note that $\varphi_{\mathcal{I}}^+(P) \sim \text{const} \times |P|^{-1/2-i\mathcal{I}/\hbar}$ has the same dependence on its argument as found in the Q -representation, which is to be expected since there is a symmetry between \hat{Q} and \hat{P} in \hat{I} .

In either case, for flux calculations it suffices to know that

$$|\varphi_{\mathcal{I}}^+(P)|^2 = \frac{e^{\sigma\pi\mathcal{I}/\hbar}}{e^{\pi\mathcal{I}/\hbar} + e^{-\pi\mathcal{I}/\hbar}} \frac{1}{|P|},$$

where we have used

$$\left| \Gamma\left(\frac{1}{2} + \frac{i\mathcal{I}}{\hbar}\right) \right|^2 = \frac{\pi}{\cosh \pi\mathcal{I}/\hbar}.$$

The I -flux across a section Σ^{out} defined by $P = P_0$ is therefore

$$\langle \psi_{\mathcal{I}}^+ /_{\Sigma^{\text{out}}} \psi_{\mathcal{I}}^+ \rangle = \sigma \frac{e^{\sigma\pi\mathcal{I}/\hbar}}{e^{\pi\mathcal{I}/\hbar} + e^{-\pi\mathcal{I}/\hbar}}$$

where here σ is the sign of P_0 . This is positive in the reactants-out channel ($P > 0$) and negative in the products-out channel ($P < 0$) which, when we remember that $\hat{\Theta}$ is defined so that upward fluxes are positive, is consistent with Figure 2. We have therefore confirmed Equation (7).

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